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Deposition of Ruthenium Nanoparticles on Carbon Aerogels for High Energy Density Supercapacitor Electrodes

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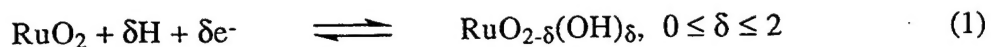
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ABSTRACT

The preparation and characterization of high surface area ruthenium/carbon aerogel composite electrodes for use in electrochemical capacitors is reported. These new materials have been prepared by the chemical vapor impregnation of ruthenium into carbon aerogels to produce a uniform distribution of adherent ≈ 20 Å nanoparticles on the aerogel surface. The electrochemically oxidized ruthenium particles contribute a pseudocapacitance to the electrode and dramatically improve the energy storage characteristics of the aerogel. These composites have demonstrated specific capacitances in excess of 200 F/g, in comparison to 95 F/g for the untreated aerogel.

INTRODUCTION

Electrochemical capacitors, or supercapacitors, are unique energy storage devices which exhibit high energy density (1-10 Wh/kg), high power density (≈ 10 kW/kg), long cycle life ($>10,000$ cycles), and operate at relatively low voltages.¹ Research on electrode materials for electrochemical capacitors has focused on two areas over the past ten years: i) high surface area polarizable materials for electric double-layer capacitors and ii) high surface area redox active materials for pseudocapacitors.² Electric double-layer capacitors (EDLCs) store energy via separation of charge across a polarized electrode/electrolyte interface. Although all materials exhibit double-layer capacitance, only those which are ideally polarizable, i.e. do not participate in faradaic reactions over the potential range of operation, are suitable for these devices.³ Carbon materials such as activated carbon,⁴ activated carbon fiber cloth (ACFC),⁵ and carbon aerogels/foams⁶ are commonly used as electrodes in EDLCs because of their attractive physical properties including high surface area and good electrical conductivity. Carbon exhibits a double layer capacitance of $10\text{-}30\text{ }\mu\text{F}/\text{cm}^2$ in aqueous electrolytes;⁷ thus, for carbons with surface areas exceeding $1000\text{ m}^2/\text{g}$, the theoretical specific capacitance approaches 150 F/g or greater. Redox supercapacitors, or pseudocapacitors, store energy via fast faradaic charge transfer reactions between a solid electrode and an electrolyte.³ Transition metal oxides such as RuO_2 ,⁸ IrO_2 ,⁹ NiO_x ,¹⁰ and conducting polymers, e.g. n- and p-doped polyaniline,¹¹ have been investigated as electrode materials for this type of device. One of the most promising candidates is hydrous ruthenium dioxide which can reversibly store $150\text{ - }260\text{ }\mu\text{F}/\text{cm}^2$ in aqueous electrolytes, or approximately 10 times the double layer capacity of carbon.⁸ This material stores charge by reversibly accepting and donating protons from an aqueous electrolyte governed by the potential dependent equilibrium of equation (1).¹²



The present paper reports the preparation and electrochemical characterization of a new type of composite electrode which utilizes carbon aerogels as high surface area substrates for pseudocapacitive RuO_2 nanoparticles. Carbon aerogels are electrically conductive (25 S/cm), low density (0.1 - 1.0 g/cc), and high surface area (400 - 1100 m^2/g) porous materials which exhibit excellent double-layer capacitance ($\approx 95 \text{ F/g}$).^{13,14} The interconnected open porosity of these materials, furthermore, can accommodate rapid mass transport of ions within the electrode, facilitating the charging and discharging of the double layer. The "aerocapacitor", an electric double-layer type capacitor utilizing two carbon aerogels as electrodes, has displayed excellent performance in 4.0 M KOH.⁶ In this paper, we demonstrate that the specific capacitance of these electrodes (typically 80-100 F/g)¹⁵ can be enhanced substantially by augmenting the double-layer capacitance of the carbon aerogels with a pseudocapacitance introduced by impregnated ruthenium oxide nanoparticles.

EXPERIMENTAL

Carbon aerogels were prepared by the catalyzed aqueous polycondensation of resorcinol and formaldehyde followed by supercritical solvent extraction and subsequent carbonization at 1050°C in N_2 .^{13,16} Monolithic rods (6 mm in diameter) of carbon aerogel ($\rho \approx 0.18 \text{ g/cc}$) were sliced into 1 mm thick disks by a diamond saw for processing and characterization. To impregnate the samples with ruthenium metal, ruthenium (III) 2,4-pentanedionate (Alfa/Aesar Co.) was placed in a 100 ml round bottom flask with the aerogels and evacuated to 5×10^{-4} torr before sealing the container. The flask was then immersed in silicone oil and heated to 190°C for two hours. The ruthenium precursor sublimates¹⁷ and impregnates the aerogel substrate. It is important to note that the aerogels

must reach a sufficiently high temperature to achieve a uniform distribution of the precursor within the sample. Upon cooling, the flask was vented and the samples were transferred to a tube furnace. The furnace was heated to 320°C under flowing argon to decompose the organometallic ruthenium precursor. The amount of metal loading in the carbon aerogels could be increased incrementally by repeating the impregnation/decomposition procedure. The ruthenium/carbon aerogel composite samples were subsequently immersed in 1.0 M H₂SO₄ and evacuated for 3 hours (5×10^{-1} torr) prior to electrochemical oxidation and characterization.

All electrochemical experiments were performed using a PAR model 273A potentiostat/galvanostat connected to a three electrode cell consisting of a carbon aerogel (or Ru/carbon aerogel composite) working electrode, a graphite counter electrode, and a standard calomel reference electrode (SCE). The carbon aerogel working electrode was contained in a Teflon® sample holder with a platinum current collector. The electrolyte was 1.0 M H₂SO₄. The deposited ruthenium nanoparticles in the composite samples were electrochemically oxidized by sweeping the voltage from open circuit potential (≈ 0.5 V) to 0.75 V vs. SCE and holding at 0.75 V for 1-2 hours, depending on the amount of Ru present.¹² The nanoparticles convert to the pseudocapacitive oxide-hydroxide form as a result of this oxidation procedure. Potentiodynamic and galvanostatic measurements were used to characterize the capacitive behavior of the new composite material. Specific surface areas of the aerogels were determined by BET gas adsorption measurements prior to electrochemical oxidation and characterization. Transmission electron microscopy (TEM) was used to examine the microstructure of the samples.

RESULTS and DISCUSSION

The deposition of ruthenium onto the surface of carbon aerogels via chemical vapor impregnation (CVI) of ruthenium (III) 2,4-pentanedionate is an effective method of achieving high metal loading in these materials. A typical treatment yielded approximately 10 % increase in weight (1.5 mg). With multiple impregnation/decomposition procedures, we have prepared samples in which the ruthenium weight exceeded that of the carbon aerogel substrate (i.e. > 100 % weight gain). Examination of these materials by TEM revealed the presence of monodisperse 20 Å ruthenium nanoparticles deposited on the surface of the carbon aerogel. Figure 1 shows the morphology of a sample with 50 % weight increase (33 wt.% Ru). The particles appear to be homogeneously distributed throughout the material and adherent to the carbon surface. Electron diffraction of these particles revealed an amorphous structure which is not surprising in view of their small size. Energy dispersive spectroscopy (EDS) confirmed their chemical identity as ruthenium. For samples with higher ruthenium loading, the number density of the particles increased, but the particle size remained relatively constant. Examination of the oxidized ruthenium particles (after electrochemical activation) indicated no apparent change in either the particle size or distribution. It is assumed that the particles increase in volume as a result of oxidation due to the difference in the bulk density of Ru (12.3 g/cc) vs. RuO₂ (6.97 g/cc)¹⁹, but the corresponding increase in particle diameter is too small to be detected within the resolution capability of the TEM.

The initial voltage sweep of the modified aerogels in 1.0 M H₂SO₄ produced a large anodic current (> 15 mA) at potentials greater than 0.7 V vs. SCE. This large current can be attributed to the electrochemical oxidation of the ruthenium in addition to some gas evolution known to occur in carbon samples with a large oxygen content under anodic polarization.¹⁸ Subsequent cycling of the samples produced a relatively symmetric potentiodynamic response centered around zero current with nearly constant

charging/discharging currents over the potential range 0 V to 0.8 V vs. SCE. A large cathodic current was generated when the voltage was swept to potentials more cathodic than 0 V vs. SCE. Researchers have attributed this response to oxygen desorption, hydrogen adsorption, and/or hydrogen evolution.¹² The capacitance for the composite samples was determined from the cyclic voltammetric sweeps by using the relationship: $C = i/v$, where i is the current response and v is the voltage sweep rate. This relationship applies only when the capacitive charging current is approximately constant over a chosen potential range. Figure 2 compares the potentiodynamic response of a ruthenium/carbon aerogel composite sample (33 wt. % Ru) with that of an untreated aerogel. The broad anodic and cathodic waves centered around +0.5 V and +0.3 V vs. SCE, respectively, are consistent with previous voltammetric measurements of RuO₂ in aqueous electrolytes.^{8,18} The results clearly indicate that the capacitance of the aerogel samples increases measurably upon the addition of ruthenium. The specific capacitance of the ruthenium/carbon aerogel composite was 206 F/g in comparison to the untreated sample which has a capacitance of 95 F/g. Moreover, the volumetric capacitance increases from 20.1 F/cc to 56.5 F/cc with the deposited Ru. These data indicate that the ruthenium nanoparticles deposited on the surface of the carbon aerogels contribute 330 F/g to the overall capacitance of the sample. This specific capacitance value is within the range of literature values for the specific capacity of RuO₂. Zheng and coworkers⁸ have reported values as high as 768 F/g. The variations of both specific and volumetric capacitance as a function of total weight percent ruthenium are shown in Figure 3 for the Ru/carbon aerogel composite electrodes. There is a relatively linear relationship between the capacitance increase and weight gain for the range examined. Characterization of samples with >100 % weight gain is in progress.

Surface area measurements of Ru/carbon aerogel composites suggest that the capacitance gain observed in these samples does not arise from an electrostatic double-layer effect. Gas adsorption surface area and capacitance data for various samples are given in Table I. The BET surface area of the composite samples decreases with increasing

amounts of Ru as one might expect since this property is normalized per unit weight (m^2/g). A more insightful comparison is to normalize the surface area per unit volume (i.e. multiplying the BET surface area by the bulk density). In this case, the different composites exhibit relatively little change in the surface area for a given volume of sample. This observation is consistent with the TEM results which show that only a small fraction of the carbon surface is covered by the ruthenium particles. The fact that there is a significant increase in electrode capacitance while the effective surface area remains relatively constant is consistent with the hypothesis that the Ru nanoparticles introduce a pseudocapacitance which is responsible for the significant increase in total electrode capacitance.

CONCLUSIONS

Chemical vapor impregnation of ruthenium into carbon aerogels produces a uniform distribution of monodisperse 20\AA particles on the aerogel surface. The oxidized Ru nanoparticles contribute significantly to the electrochemical capacitance of the resulting composite samples by introducing a pseudocapacitance which arises from faradaic reactions of the deposits. The specific capacitance of these new composite materials, with values in excess of 200 F/g , is more than double the capacitance of the untreated sample, while the volumetric capacity is nearly triple the original value.

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Table I. Comparison of surface area and capacity data for different compositions of Ru/carbon aerogel composite electrodes.

weight % ruthenium	BET surface area (m ² /g)	"volumetric" surface area (m ² /cc)	specific capacity (F/g)	volumetric capacity (F/cc)
0	724	129	85	20.09
12.09	546.1	106.4	95.8	25
18.5	486.8	102.4	138.6	30.25
28.7	452.5	107.6	174.9	43.66
34.93	434.5	110.5	206.4	55.09

FIGURE CAPTIONS

- Figure 1. Transmission electron micrograph of the Ru/carbon aerogel composite sample showing ≈ 20 Å diameter nanoparticles embedded in the amorphous carbon aerogel structure.
- Figure 2. Cyclic voltammogram of Ru/carbon aerogel composite electrode in 1.0 M H₂SO₄ compared to the response for an untreated aerogel sample. Sweep rate: 2.0 mV/sec. The ordinate axis for this plot has *not* been normalized (per unit weight or area) to emphasize the magnitude of the capacity increase for a particular sample. Both samples were nearly identical in mass before processing.
- Figure 3. The effect of ruthenium loading on the specific capacity and volumetric capacity of Ru/carbon aerogel composite electrodes.

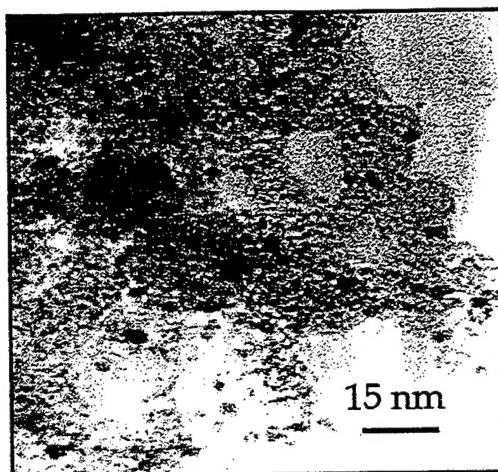


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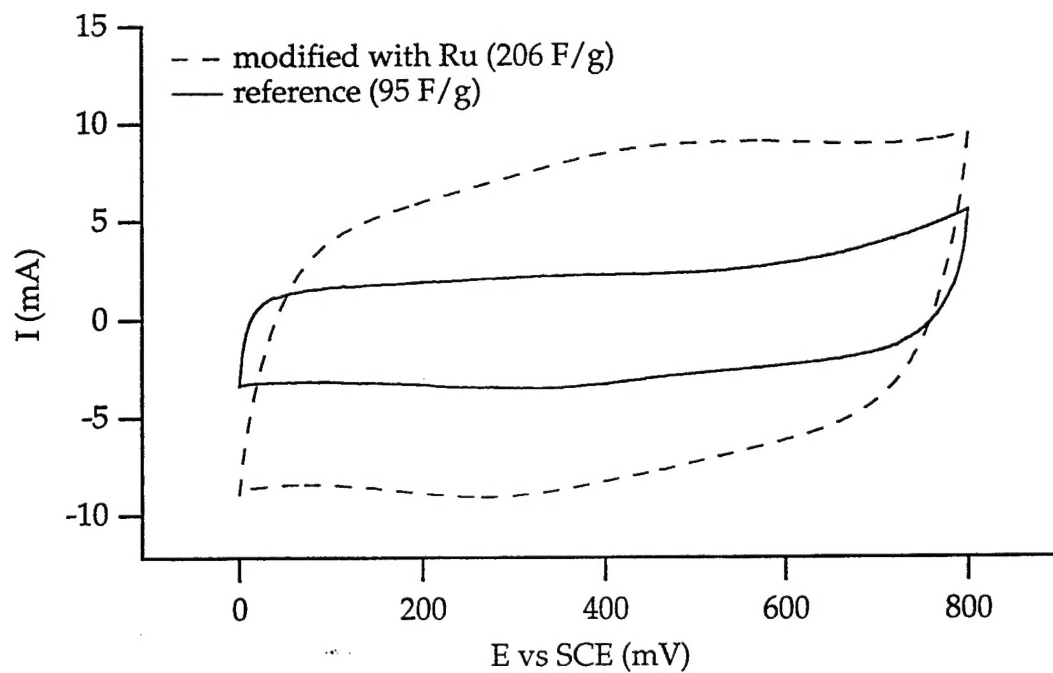


Figure 2. Cyclic voltammogram of Ru/carbon aerogel composite electrode in 1.0 M H_2SO_4 compared to the response for an untreated aerogel sample. Sweep rate: 2.0 mV/sec. The ordinate axis for this plot has *not* been normalized (per unit weight or area) to emphasize the magnitude of the capacity increase for a particular sample. Both samples were nearly identical in mass before processing.

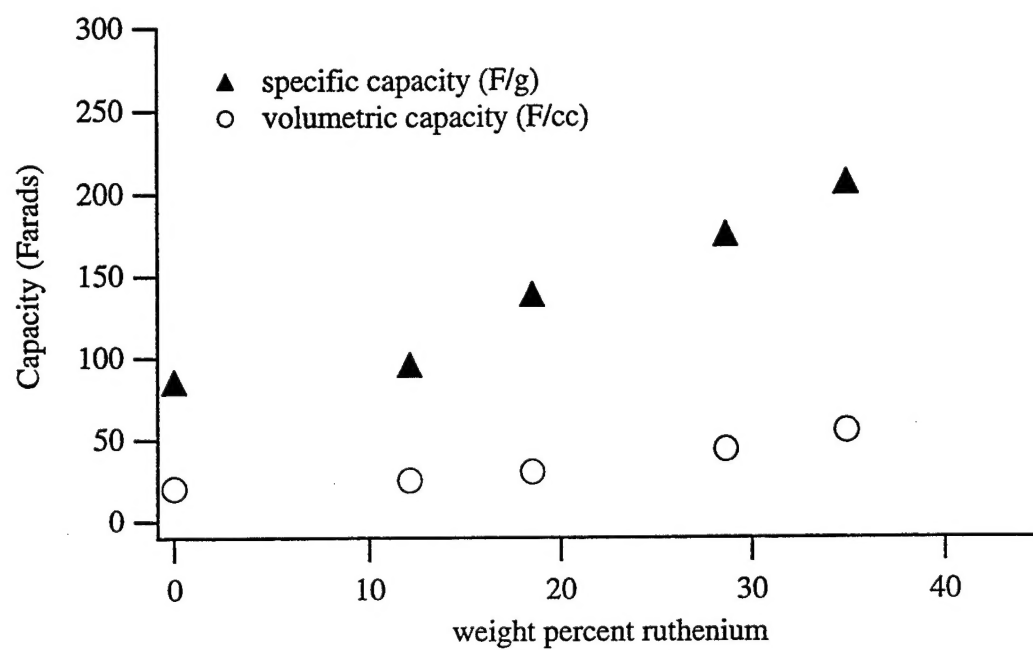


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